

Electrophoretic fabrication of LiCoO₂ positive electrodes for rechargeable lithium batteries

Kiyoshi Kanamura*, Atsushi Goto, Young Ho Rho, Takao Umegaki

Department of Applied Chemistry, Graduate School of Engineering, Tokyo Metropolitan University,
1-1 Minami-Osawa, Hachioji, Tokyo 192-0397, Japan

Received 20 June 2000; accepted 7 January 2001

Abstract

LiCoO₂ composite electrodes for rechargeable lithium batteries were fabricated by an electrophoretic deposition (EPD) method. LiCoO₂ oxide particles were deposited on an Al current collector with appropriate amounts of Ketjen black and polytetrafluoroethylene (PTFE) by applying a high dc voltage between two electrodes in an EPD suspension. The density of the composite electrode was comparable with that for an electrode prepared by a conventional process. The LiCoO₂ electrode exhibited an initial discharge capacity of 142 mAh g⁻¹. The cycleability of the LiCoO₂ electrode prepared by the EPD was also equivalent to those of pellet type electrodes. From these results, it is concluded that the EPD method can be applied as the practical electrode fabrication process for a rechargeable lithium battery.

© 2001 Elsevier Science B.V. All rights reserved.

Keywords: Electrophoretic deposition; Rechargeable lithium battery; Fabrication of electrodes

1. Introduction

Electrophoretic deposition (EPD) has been investigated as preparation methods for thin films of functional materials on various kinds of substrates [1–8]. The EPD generally proceeds via three steps: (1) particle charging; (2) particle transportation via a voltage difference; (3) deposition of particles with discharge. Most of studies on the EPD processes have been concerned with deposition of non-conducting ceramics, such as Al₂O₃, BaTiO₃, Ca₁₀(PO₄)₆(OH)₂, and PbZrO₃ which are used in various kinds of novel devices. The thin films of these compounds have been successfully prepared by the EPD method.

Positive and negative electrodes used in rechargeable lithium batteries are manufactured through following processes: (1) mixing of active materials, conducting additives, and binding materials in an organic solvent to make a paste; (2) painting of the paste on an Al current collector; (3) evaporating the organic solvent; (4) pressing the electrode. These processes must be optimized to obtain a high-performance rechargeable lithium battery. Specially, a high discharge capacity at a high-rate use is attained under the optimized fabrication conditions of electrodes for

rechargeable lithium batteries. In an industrial process, the conditions are precisely controlled to obtain a good electrode structure, which is realized by a uniform distribution of materials, a uniform thickness of electrode, a proper density of electrode, and so on. Therefore, we prepared a LiCoO₂ electrode by using the EPD method, and its electrochemical performance was tested as a positive electrode of a rechargeable lithium battery. The optimized conditions for the EPD were determined in this study.

2. Experimental

LiCoO₂, Ketjen black, and polytetrafluoroethylene (PTFE) were dispersed in an acetone solution with a small amount of I₂. LiCoO₂ powder was synthesized by heating a mixture of Li₂CO₃ and CoCO₃ with a molar ratio of 1:2 at 800°C for 24 h in air. The crystal structure of the synthesized powder was assigned to LiCoO₂ with an X-ray diffraction method [9–12]. Ketjen black and PTFE were used as conducting and binding materials, respectively. A solvent of the EPD was an acetone solution. Three materials were suspended in the acetone solution. The particles should have a surface charge to realize their good EPD characteristics. By the way, it has been reported that an addition of iodine produces charged particles in the solution through chemical

* Corresponding author. Tel.: +81-426-77-2827; fax: +81-426-77-2827.
E-mail address: kanamura-kiyoshi@c.metro-u.ac.jp (K. Kanamura).

reaction of I_2 with acetone [5]. In this study, I_2 was added into the suspension for the EPD process. An Al foil was used as a substrate, and a stainless steel sheet was used as a counter electrode. The working and counter electrodes were separated with a distance of 10 mm. The voltage difference between two electrodes was set at 100 V (electric field: 100 V cm^{-1}), and the EPD duration was 1 min. The EPD process was repeated (2–4 times), until the deposit mass increased to 10 mg. After the EPD process, the weight increment of the substrate was measured to determine the weight of deposits. Then, the substrate was heated at 800°C to eliminate PTFE and Ketjen black in order to determine the weight of LiCoO_2 deposited by the EPD process.

The electrochemical performance of the LiCoO_2 electrode was investigated by using a discharge and charge cycle test at $0.1C$ rate. A pellet type LiCoO_2 electrode was also prepared by pressing a mixture of LiCoO_2 , Ketjen black, and PTFE with a weight ratio of 80:15:5 at 50 MPa. This pellet was pressed into a Ti mesh as a current collector. Lithium metal was used as counter and reference electrodes. The electrolyte was a mixed solvent of ethylene carbonate (EC) and diethyl carbonate (DEC) with a volume ratio of 1:1 containing 1.0 mol dm^{-3} LiClO_4 . The EPD process was conducted in the acetone solution containing various amounts of I_2 , Ketjen black, PTFE, and LiCoO_2 in order to optimize the suspension contents for realizing the best electrochemical performance of the LiCoO_2 electrode. All electrochemical experiments were carried out under argon atmosphere and at room temperature.

3. Results and discussion

LiCoO_2 powders were prepared by a solid state reaction of Li_2CO_3 and CoCO_3 at 800°C for 48 h under air atmosphere. All peaks in the X-ray diffraction pattern were assigned to appropriate Miller indices based on a layered rock salt structure ($Fd\bar{3}m$). By the way, a particle size is one of important parameters for FPD process. In general, a smaller particle migrates more easily than a larger one, when both particles have the same surface charge. This means that small particles are selected in the course of a deposition on a substrate in the EPD process. This selection is one of good advantages for a preparation of positive and negative electrodes for rechargeable lithium batteries. The prepared LiCoO_2 particle had a distribution of a few μm to $10 \mu\text{m}$ in diameter.

The weight increment of the Al substrate during the first EPD process was measured under various concentrations of I_2 in the suspension. The deposition of LiCoO_2 , Ketjen black, and PTFE was enhanced by the addition of I_2 . The amount of 10 mg I_2 in 50 ml acetone was enough for high deposition rate during the EPD process. In this experiment, the amounts of LiCoO_2 , Ketjen black, and PTFE were 500, 0–50, and 12–48 mg, respectively. In all following experiments, the amount of I_2 was set to be 10 mg.

Fig. 1 shows the scanning electron micrographs of the LiCoO_2 electrodes prepared by the EPD process under various amounts of Ketjen black. The amount of LiCoO_2 and PTFE were 500 and 24 mg in the EPD suspension,

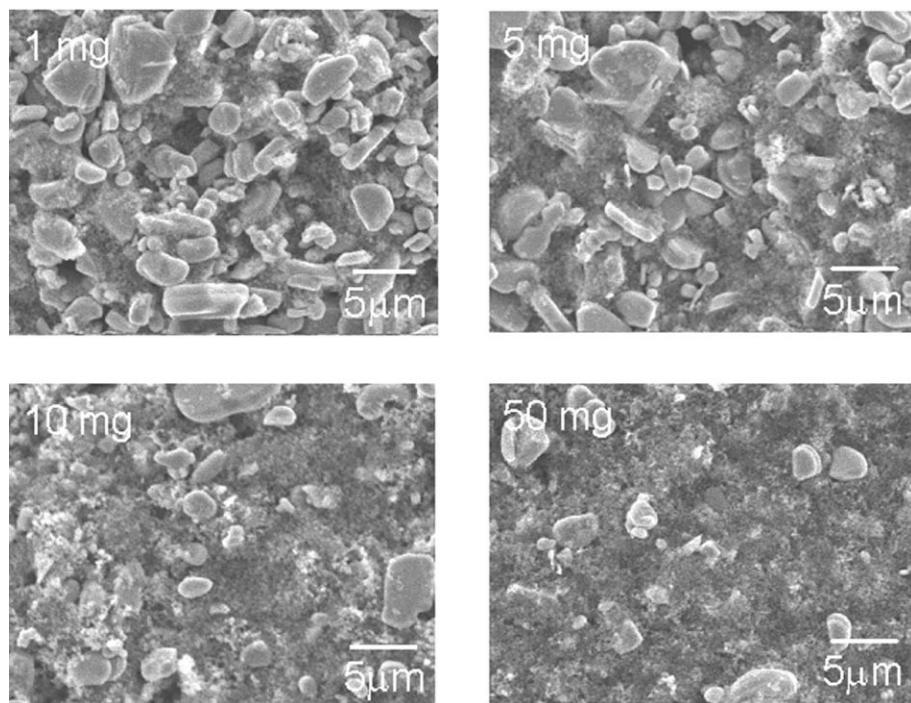


Fig. 1. Scanning electron micrographs of the LiCoO_2 electrodes prepared by the EPD process under various amount of Ketjen black content in acetone–iodine solution.

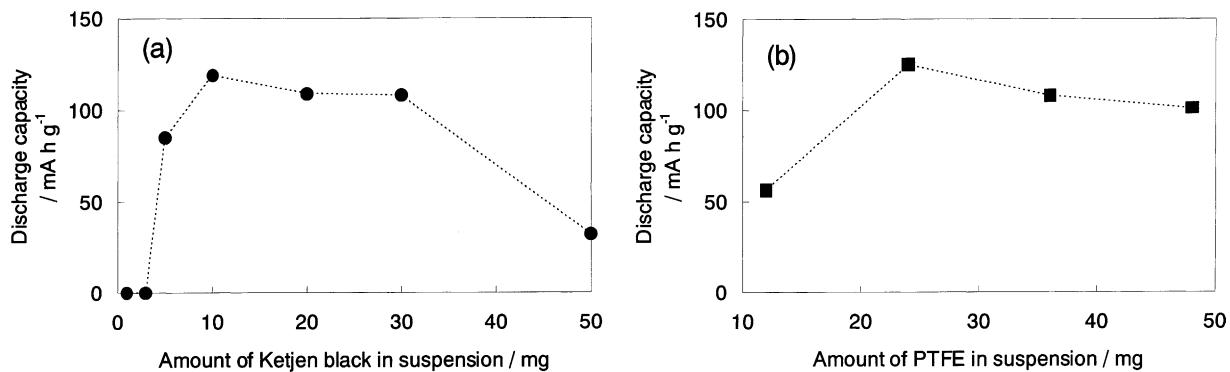


Fig. 2. Dependence of the discharge capacity of the LiCoO_2 electrode on (a) the amount of PTFE; (b) the amount of Ketjen black contents in acetone–iodine solution.

respectively. The amount of LiCoO_2 particle in the electrode decreased with increasing amount of Ketjen black in the suspension. On the other hand, the amount of Ketjen black in the electrode increased with increasing amount of Ketjen black in the suspension. Thus, the contents of LiCoO_2 , Ketjen black, and PTFE strongly depended on the EPD suspension. Of course, the discharge capacities of these electrodes may depend on the EPD conditions. The deposited LiCoO_2 particle size was less than $5 \mu\text{m}$, which was smaller than those of the starting powders. The larger LiCoO_2 particles were eliminated during the EPD process. The electrode surface was very smooth, indicating that a homogeneous deposition took place during the EPD process. This is due to the uniform dispersion of all materials in the acetone solution.

When the EPD process was performed in the suspension containing various amounts of PTFE, the amount of LiCoO_2 decreased with increasing amount of PTFE. On the other hand, the amount of Ketjen black increased with increasing amount of PTFE in the suspension. This means that the EPD process of each material does not proceed, independently. Probably, LiCoO_2 , Ketjen black, and PTFE interact each other in the suspension. Probably, Ketjen black and PTFE are adsorbed on the LiCoO_2 particles. The surface morphology of the LiCoO_2 electrodes was similar to those in Fig. 1.

Fig. 2 shows the dependence of the discharge capacity of the $[\text{LiCoO}_2/1.0 \text{ M LiClO}_4/(\text{EC} + \text{DEC})/\text{Li metal}]$ cell on the amounts of Ketjen black and PTFE in the suspension. The specific discharge capacities plotted in this figure were

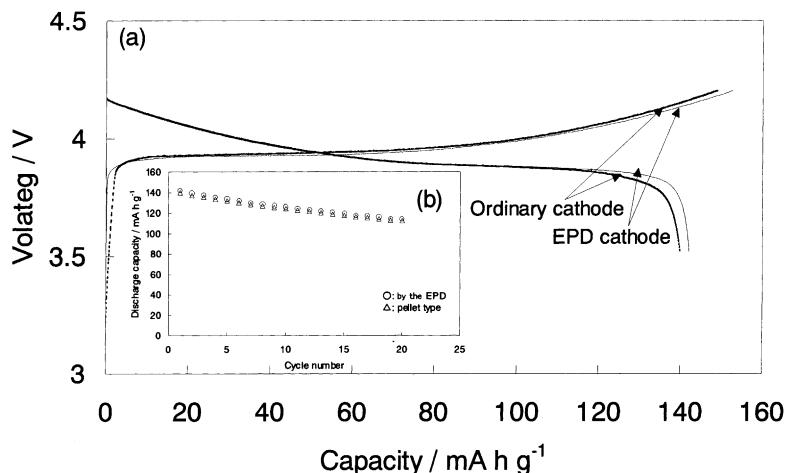


Fig. 3. (a) Discharge and charge curves of LiCoO_2 fabricated by the ordinary and the EPD processes at 0.1C rate in $1.0 \text{ mol dm}^{-3} \text{ LiClO}_4/\text{EC} + \text{DEC}$; (b) discharge capacity changes of LiCoO_2 fabricated by the EPD and the ordinary processes.

Table 1
Optimized conditions of the EPD for the fabrication of LiCoO_2 electrode^a

Active material	Conducting material	Binder	Solvent	Additive
LiCoO_2 (500 mg)	Ketjen black (10 mg)	Teflon [®] (24 mg)	Acetone (50 ml)	Iodine (10 mg)

^a EPD conditions: 100 V cm^{-1} for 1 min.

calculated, based on the total weight of the deposits (LiCoO_2 , Ketjen black, and PTFE). The maximum discharge capacity was obtained at 10 mg Ketjen black and 24 mg PTFE, respectively. This is due to the dependence of the electrode performance on the ratio of the amounts of LiCoO_2 , PTFE, and Ketjen black. Because, the LiCoO_2 electrode should have high ionic and electronic conductivities at the highest content of LiCoO_2 particle. In the following experiments, the LiCoO_2 electrode prepared under the optimized conditions in Table 1 was used.

The LiCoO_2 weight in the electrode prepared under the optimized conditions was 9.1 mg, which corresponds 89% of the total deposit weight. This value was determined from the weight difference before and after heating the deposits in air at 800°C. Ketjen black and PTFE were disappeared during this heat treatment. The apparent densities of these deposits were estimated from the electrode thickness and they were similar to those for the pellet electrodes prepared in this study.

Fig. 3(a) shows the discharge and charge curves for the LiCoO_2 electrode prepared by the EPD and the standard method described in the experimental section in EC + DEC with 1.0 mol dm^{-3} LiClO_4 electrolyte at the 0.1C rate. The discharge and charge curves for the LiCoO_2 electrode prepared by the EPD were very similar to that of the pellet type electrode. This result clearly indicates that the EPD method is suitable for the fabrication of the LiCoO_2 positive electrode. The discharge capacity of the LiCoO_2 electrode obtained by the EPD was 142 mAh g^{-1} based on only active material. These values are near to the reported capacity in the potential range from 3.5 V versus Li/Li^+ and 4.2 V versus Li/Li^+ [9–12].

Fig. 3(b) shows the discharge capacity change for the LiCoO_2 electrode during the discharge and charge cycle in EC + DEC with 1.0 mol dm^{-3} LiClO_4 electrolyte at 0.1C rate. The discharge capacity change for the LiCoO_2 electrode prepared by the EPD was comparable to that for the pellet type electrode. This indicates that the LiCoO_2 electrode prepared by the EPD has an enough high cycleability as a positive electrode of rechargeable lithium battery.

4. Conclusions

The LiCoO_2 electrodes were successfully fabricated by using the EPD. The EPD suspension contained particles of LiCoO_2 , Ketjen black, and PTFE dispersed in the acetone–iodine solution. All dispersed particles were transported to a cathode (Al foil) and deposited on it when a dc voltage was applied between two electrodes soaked in the suspension. A uniform electrode with a smooth surface was prepared by the EPD. The total fabrication time for positive electrodes was <5 min. The high electrode performance was realized by optimizing the amounts of dispersed particles in the EPD suspension.

Acknowledgements

This work was partially funded by CASIO SCIENCE PROMOTION FOUNDATION.

References

- [1] P. Sarkar, P.S. Nicholson, *J. Am. Ceram. Soc.* 79 (1996) 1987.
- [2] P.M. Biesheuvel, H. Verweij, *J. Am. Ceram. Soc.* 82 (1999) 1451.
- [3] E.M. Wong, P.C. Searson, *Appl. Phys. Lett.* 74 (1999) 2939.
- [4] Y. Tokuoka, T. Kishi, T. Nagai, *Denki Kagaku* 42 (1974) 80.
- [5] N. Koura, T. Tsukamoto, H. Shoji, T. Hotta, *Jpn. J. Appl. Phys.* 34 (1995) 1643.
- [6] T. Ishihara, K. Sato, Y. Takita, *J. Am. Ceram. Soc.* 79 (1996) 913.
- [7] K. Yamashita, M. Nagai, T. Umegaki, *J. Mater. Sci.* 32 (1997) 6661.
- [8] J. Hamagami, Y. Inda, K. Yamashita, T. Umegaki, *Solid State Ionics* 113–115 (1998) 235.
- [9] T. Ohzuku, A. Ueda, *J. Electrochem. Soc.* 144 (1997) 2780.
- [10] G.C. Amatucci, J.M. Tarascon, L.C. Klein, *J. Electrochem. Soc.* 143 (1996) 1114.
- [11] G.G. Amatucci, J.M. Tarascon, D. Larcher, L.C. Klein, *Solid State Ionics* 84 (1996) 169.
- [12] R.J. Gummow, M.M. Thackeray, W.I.F. David, S. Hull, *Mater. Res. Bull.* 27 (1992) 327.